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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B22D 23/00, B22F 9/08, C22F 1/08

A1

(11) International Publication Number: WO 90/11852

(43) International Publication Date: 18 October 1990 (18.10.90)

(21) International Application Number: PCT/US90/01737

(22) International Filing Date: 2 April 1990 (02.04.90)

(30) Priority data:

332,181	3 April 1989 (03.04.89)	US
Not furnished	30 March 1990 (30.03.90)	US

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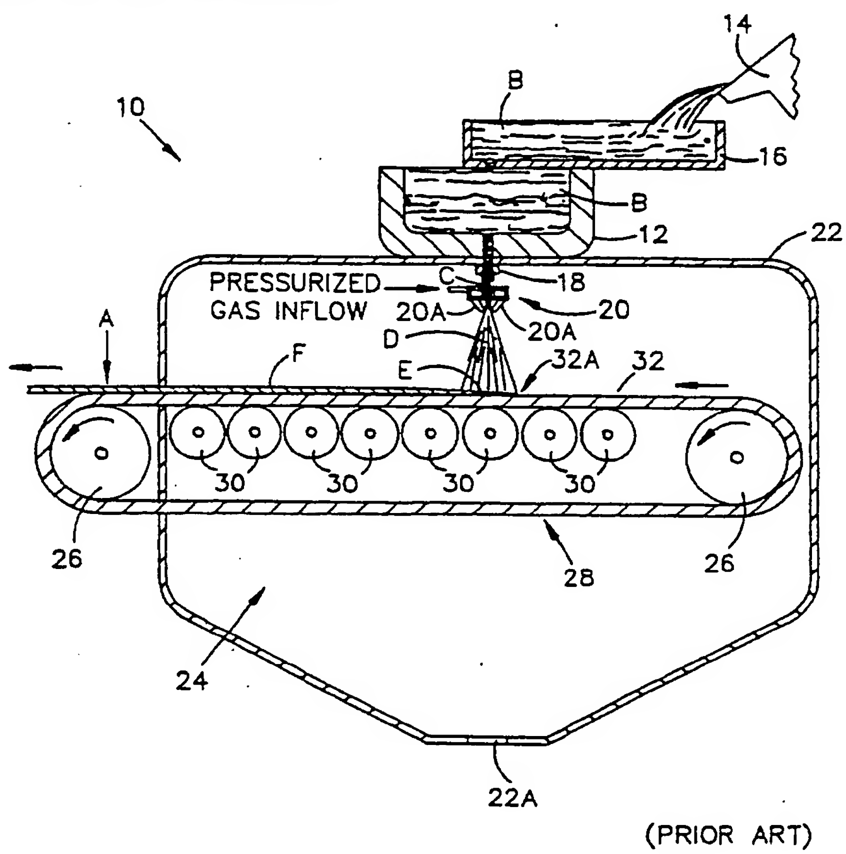
(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), + CH (European patent), CM (OAPI patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD OF TREATING SPRAY CAST METAL DEPOSITS

(57) Abstract

A method of treating spray cast metal strip, especially of copper alloys, to reduce porosity. The deposited strip (A) is subjected to a cold rolling reduction of at least about 25 % and then annealed at a temperature of from about 450° to about 800°C for about 1 to about 8 hours.



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"METHOD OF TREATING SPRAY CAST METAL DEPOSITS"

This invention relates generally to the treatment of metal alloys produced by spray casting. More particularly, this invention relates to a method of treating spray cast metal deposits to reduce the porosity thereof.

Spray casting is a method of manufacturing metal or metal alloy articles directly to a desired shape. The basic spray casting process comprises the steps of atomizing a fine stream of molten metal, depositing the particles onto a collector where the hot particles solidify to form a preform and then working or directly machining the preform to generate the final shape and/or properties required.

One form of such a spray casting process is generally known as the OSPREY process and is more fully disclosed in U.S. Patent Numbers RE 31,767 and 4,804,034 as well as United Kingdom Patent No. 2,172,900. Further details about the process are contained in the publication entitled "The Osprey Preform Process" by R. W. Evans, et al, Powder Metallurgy, Vol. 28, No. 1 (1985).

In the OSPREY process, a controlled stream of molten metal is poured into a gas-atomizing device where it is impacted by high-velocity jets of gas, usually nitrogen or argon. The resulting spray of metal particles is directed onto a "collector" where the hot particles re-coalesce to form a highly dense preform. The collector is fixed to a mechanism which is programmed to form a sequence of movements within the spray, so that the desired preform shape can be generated. The preform can then be further processed, normally by hot working, to form a semi-finished or finished product.

The OSPREY process has also been proposed for producing strip or plate or spray-coated strip or plate as disclosed in U.S. Patent No. 3,775,156 and European Patent Application No. 225,080. For producing these products, a substrate or collector such as a flat substrate or an endless belt is moved continuously through the spray to receive a deposit of uniform thickness across its width.

While spray cast products have many desirable properties, one of the drawbacks to the use of the process, especially in making thin gauge strip material, is that the spray cast product has a relatively high degree of porosity. For example, in the case of spray cast copper alloy C-194, it has been found to contain from about 1% to about 10% by volume of pores. It is theorized that most of these pores contain nitrogen gas which has been entrapped during the casting process. Upon cold rolling the material after the spray cast process, the pores or defects are collapsed and elongated in the direction of rolling. These defects may be expected to have a detrimental effect on ductility and such ductility related mechanical properties as lead bend fatigue life and bend formability. These properties are important, especially in the case of copper based alloys which have application in the electrical and electronic industry. Thus, the pores or the effect of such pores must be minimized in order for the spray cast process to be satisfactorily used for the casting of such alloys.

Several schemes for improving the density of spray cast articles have been disclosed. U.S. Patent No. RE31,767, discloses subjecting the article to a subsequent densification process such as drop forging. U.S. Patent No. 3,775,156 discloses passing a spray cast strip through a rolling mill to reduce porosity.

One object of the present invention is the provision of a method for treating spray cast material to reduce porosity.

A more specific object of the present invention is the provision of a method for treating spray cast strip material which results in a reduction of defects due to porosity.

The objects and advantages of the present invention are achieved, in accordance with the present invention, by spray casting a strip of metal by atomizing a molten stream of metal and depositing the atomized particles onto a moving substrate to form a strip. The resulting deposit is then cold worked as by cold rolling to a reduction at which the pores are substantially collapsed and elongated forming planar defects. The strip is then annealed at a temperature and time to heal a significant portion of the planar defects. Such anneal may be from about 1 to about 8 hours at a temperature of at least 450°C. It has been surprisingly found that after the cold working and anneal, the frequency of defects due to the presence of pores is drastically reduced.

These and other features and advantages of the present invention will become more apparent to those skilled in the art upon reading the following detailed description taken in conjunction with the accompanying drawings in which:

Figure 1 is a schematic view, partly in section, of a prior art spray-deposition apparatus suitable for producing a thin gauge strip product on a moving substrate;

Figure 2 is a photomicrograph taken at a magnification of 250X of a spray cast product showing a typical cross-sectional area as cast;

Figure 3 is a photomicrograph, taken at 250X magnification, of a longitudinal section of the sample of Figure 2 after the sample has been cold rolled to a 74% reduction;

Figure 4 is a photomicrograph, taken at 250X magnification, of a transverse section of the sample of Figure 2, after it has been cold rolled to a 74% reduction; and

Figure 5 is a photomicrograph of a longitudinal section of the sample of Figure 2 magnified 250X, and taken after the sample has been cold rolled to a 74% reduction and subjected to a 500°C/4 hr. anneal.

Referring to the drawings, Figure 1 discloses a spray deposition apparatus 10 as known in the art. The system as illustrated produces a continuous strip of a product A. One example of a suitable metal B is a copper alloy.

The spray deposition apparatus 10 employs a tundish 12 in which a metal alloy having a desired composition B is held in molten form. The tundish 12 receives the molten alloy B from a tiltable melt furnace 14, via a transfer launder 16. The tundish 12 further has a bottom nozzle 18 through which the molten alloy B issues in a continuous stream C. A gas atomizer 20 is positioned below the tundish bottom nozzle 18 within a spray chamber 22 of the apparatus 10.

The atomizer 20 is supplied with a gas under pressure from any suitable source. The gas serves to atomize the molten metal alloy and also supplies a protective atmosphere to prevent oxidation of the atomized droplets. A most preferred gas is nitrogen. The nitrogen should have a low concentration of oxygen to avoid the formation of undesirable oxides. An oxygen concentration of under about 100 ppm and preferably less

than about 10 ppm may be used. The atomizer 20 surrounds the molten metal stream C and has a plurality of jets 20A from which the gas exits to impinge on the stream C so as to convert the stream into a spray D comprising a plurality of atomized molten droplets. The droplets are broadcast downwardly from the atomizer 20 in the form of a divergent conical pattern. If desired, more than one atomizer 20 may be used. The atomizer(s) 20 may be moved in a desired pattern for a more uniform distribution of the molten metal particles.

A continuous substrate system 24 as employed by the apparatus 10 extends into the spray chamber 22 in generally horizontal fashion and spaced in relation to the gas atomizer 20. The substrate system 24 includes a drive means comprising a pair of spaced rolls 26, and endless substrate 28 in the form of a flexible belt entrained about and extending between the spaced rolls 26 and a series of rollers 30 which underlie and support an upper run 32 of the endless substrate 28. An area 32A of the substrate upper run 32 directly underlies the divergent pattern of spray D. The area 32A receives a deposit E of the atomized metal particles to form the metal strip product A.

The metal strip product A of the desired alloy may be milled on its top and bottom surface to remove surface oxides. In accordance with the present invention, the milled strip may then be cold rolled to a suitable reduction so that the pores present in the material are substantially collapsed to form planar defects elongated in the directions of cold rolling. Such reduction should be preferably at least 25% up to about 85% and more preferably 50% to about 75%.

After the cold rolling reduction, the strip should be annealed, to heal a substantial portion of such defects. Preferably such anneal is a bell anneal, at a temperature of from about 450°C and more preferably

at least from about 500°C up to about 800°C. The time of the anneal should be sufficient to heal a substantial portion of the planar defects at the temperature of the anneal. Preferably, the time is from about 1 to about 8 hours and more preferably from about 2 to about 6 hours. The strip may then be further processed in any conventional manner.

As indicated above, a suitable type of metal which may be spray cast by the apparatus described above and treated in accordance with the present invention is a copper alloy. By way of example, one particular copper alloy is copper alloy C19400. Generally, this alloy is a copper based alloy containing from about 1.5 to about 3.5% iron and small amounts of zinc and phosphorous. This alloy is more specifically described in U.S. Patent 3,522,039 to C. D. McLain. As described in that patent, the alloy generally comprises 1.5 to 3.5% iron, from 0.01 to 0.15% phosphorous, from 0.03 to 0.20% zinc and the balance essentially copper. Generally, strip of this alloy is produced by casting it in molten form into a short rectangularly shaped mold which initially is closed at one end by a plug on a removable ram or starter bar. The metal freezes to the plug and forms a shell against the mold surface. The ram is then steadily withdrawn, pulling the shell with it. As the shell exits from the bottom of the mold, cold water is sprayed on it, cooling it rapidly and causing the contained molten metal to freeze. In this manner a continuously cast slab of the desired length is produced. The cast slab is then hot worked into strip form and further treated to final thickness.

In accordance with the teachings of the present invention, copper alloy C19400 was cast as thin gauge strip utilizing a spray casting process as described above. According to the spray cast process,

the molten metal was caused to flow through an atomizer where nitrogen gas served to atomize the molten metal alloy into droplets which were broadcast downwardly from the atomizer onto a moving substrate forming a strip of material.

Five samples of the spray cast alloy C19400 having the compositions set forth in Table I below were processed by milling to 0.150 inch thickness to remove surface oxides and then annealing at 550°C for 4 hours followed by a cold rolling reduction of about 74% to about 0.039 inch thickness. All the samples contained several hundred pores per square millimeter in the "as cast" condition as set forth in Table II reproduced below. Even after cold rolling to the 0.039 inch thickness, similar defect frequencies were seen on the longitudinal and transverse metalographic sections as shown in Table II.

Table I

Compositions - Weight %

Sample	Fe	P	Zn
1	2.13	0.026	.12
2	2.12	0.027	.12
3	1.66	0.017	.13
4	1.66	0.014	.13
5	1.63	0.016	.13
Control	2.35	.020	.095

Table II

Pore Sizes and Frequencies

Sample	Pore or Defect Frequency Number/mm^2	Mean Size Microns	Volume Percent
	As-Cast		
1	368	7.0	2.1
2	309	10.3	4.1
3	324	8.0	2.7
4	226	12.3	5.5
5	260	12.3	6.0
	Cold Rolled 74%, Transverse Section		
1	528	9.7	
2	361	12.7	
3	390	12.9	
4	394	17.9	
5	373	17.4	
	Cold Rolled 74%, Longitudinal Section		
1	185	29.7	
2	157	32.2	
3	51	52.0	
4	45	54.6	
5	47	49.1	

Referring now to Figures 2-5, such Figures are photomicrographs of sample 1 at various stages of treatment taken at a magnification of 250X. The samples were etched to enhance the porosity. The etching solution consisted of 20 ml water, 20 ml ammonium hydroxide and 5 ml hydrogen peroxide.

Figure 2 shows a typical longitudinal cross-sectional area of sample 1, in the "as cast" condition, at a magnification of 250X. With the microscopic field view of 115 x 90 mm at a magnification of 250X the actual area shown is about 0.166 mm . As can be seen, there are a substantial number of pores within the magnified area.

Figure 3 is a photomicrograph at a magnification of 250X of a typical area of a longitudinal section of sample 1 after the milled sample was annealed at 550°C for 4 hours and then cold rolled to a 74% reduction down to 0.039 inch. Figure 4 is a photomicrograph of a transverse section of sample 1 after the same treatment. As will be noted, even the cold working does not eliminate the defects. However, the defects after cold working are in the form of elongated, generally planar defects. The size and frequency of these defects for the various samples are set forth in Table II.

Figure 5 is a photomicrograph at 250X magnification of sample 1 taken through a longitudinal section of a typical area after the sample has been subjected to a 500°C/4 hour anneal after the cold rolling. As will be noted, the frequency of the defects visible at a magnification of 250X is drastically reduced, although there still are a few defects present. This held true for all of the samples. At 250X magnification, the defect frequency after cold working and the 500°C/4 hour anneal was too low to provide any meaningful measurement, but was at least one to two orders of magnitude lower than those shown in Table II.

A control sample having a composition as set forth in Table I was cast and hot worked according to the conventional process. The hot rolled plate was cold

rolled 58% to 0.150 inch and then subjected to a 550°C/4 hour anneal followed by a 74% cold rolled reduction to 0.039. The control sample was further annealed at 500°C for 4 hours followed by a 72% cold rolled reduction to 0.011 inch.

The spray cast samples of Table I were further treated to final gauge after the 500°C/4 hour anneal by cold rolling 72% to 0.011 inch.

Table III sets forth the mechanical properties of the spray cast material samples as well as the control sample after the above treatment.

Table III

Mechanical Properties at 0.011" Gauge (Longitudinal Orientation)

Code No.	0.2% Yield Strength, ksi	Tensile Strength, ksi	Minimum Bend Radius/ Thickness	Mean Lead Bend Fatigue Life, Cycles
Control	71.3	73.7	1.5	6.5
1	71.4	74.2	2.0	6.5
2	71.9	75.1	1.3-1.5	6.2
3	70.7	73.3	2.1	6.4
4	69.8	71.1	1.2-1.4	5.9
5	69.5	72.2	1.3-1.5	5.9

As will be noted from Table III, the mechanical properties of the spray cast material at final gauge were equivalent to that of the control material.

It is thus seen that by a combination of cold rolling followed by annealing at a temperature where diffusion is sufficiently rapid, most of the large

planar defects present in spray cast plus cold rolled alloys can be transformed into much smaller voids which have less of a detrimental effect on the mechanical properties. While this technique is thought applicable to spray cast metal alloys in general, it has special applicability to copper alloys.

Other alloys which have been treated include Copper Alloy C51000 and Copper Alloy C71300. Alloy C51000 is a copper base alloy containing from about 3.5 to about 5.8% tin, from about 0.03 to about 0.35% phosphorous, up to about 0.05% lead, up to about 0.30% zinc, up to about 0.10% iron, and the balance essentially copper. Alloy C71300 is a copper base alloy containing from about 23.5 to about 26.5% nickel, up to about 1.0% manganese, up to about 1.0% zinc, up to about 0.20% iron, up to about 0.25% lead, and the balance essentially copper.

Table IV below sets forth the nominal composition of various copper base alloys that have been treated in accordance with the present invention.

TABLE IV

Sample	Alloy	Nominal Composition
1	C19400	Cu - 2.0% Fe
2	C19400 + Si	Cu - 2.0% Fe - 0.5% Si
3	C19400 + Al	Cu - 2.0% Fe - 0.5% Al
4	C713	Cu - 25% Ni
5	C510	Cu - 5.0% Sn - 0.1% P
6	Cu - Al - Si	Cu - 2.8% Al - 1.8% Si

The following Table V sets forth the mean pore size and frequency of pores of the various Samples set forth in Table IV after spray casting, but before any subsequent treatment. The as-cast porosity size distribution was measured using a magnification of 1620X on the video monitor.

TABLE V

Pore Sizes and Frequencies - As Cast

Sample	Pore or Defect Frequency Number/mm^2	Mean Size Mircons (X Proj/Y Proj.)
1	880	6.1/6.5
2	336	6.8/8.0
3	662	6.0/5.7
4	757	10.9/12.4
5	701	1.6/1.8
6	128	8.5/9.5

Samples of the various alloys set forth in Table IV were further processed according to the various conditions set forth in Table VI. As indicated, some of the samples were annealed at 500°C for four hours after being spray cast, while this annealing step was omitted for other samples. All samples were cold rolled to either an 85% or an 82% reduction in the manner indicated in Table VI. Thereafter, some of the samples were further treated by an anneal at 700°C for four hours while this step was omitted for other samples as indicated.

Table VII below sets forth the pore or defect size and frequencies for the samples tested under the conditions set forth in Table VI. For these measurements a magnification of 672X was used. All samples except Sample 6 were etched with a solution of 44% water, 44% ammonium hydroxide and 12% hydrogen peroxide. Sample 6 was etched with an ASM #4 etchant.

TABLE VI

Treatment Code

<table>
<tr><th>Condition</th><th>Treatment</th></tr>
<tr><td>1</td><td>No Anneal|85% total Reduction, <10% per pass</td></tr>
<tr><td>2</td><td>500°C/4 hrs.|85% total Reduction, <10% per pass</td></tr>
<tr><td>3</td><td>No Anneal|85% total Reduction, < 10% per pass|700°C/4 hrs.</td></tr>
<tr><td>4</td><td>500°C/4 hrs.|85% total Reduction, < 10% per pass|700°C/4 hrs.</td></tr>
<tr><td>5</td><td>No Anneal|82% total Reduction, < 10% per pass</td></tr>
<tr><td>6</td><td>500°C/4 hrs.|82% total Reduction, 10-20% per pass</td></tr>
<tr><td>7</td><td>No Anneal|82% total Reduction, 10-20% per pass|700°C/4 hrs.</td></tr>
<tr><td>8</td><td>500°C/4 hrs.|82% total Reduction, 10-20% per pass|700°C/4 hrs.</td></tr>
<tr><td>9</td><td>500°C/4 hrs.|82% Reduction in one pass|700°C/4 hrs.</td></tr>
</table>

TABLE VII

Pore Sizes and Frequencies

Sample	Condition	Pore or Defect Frequencies Number/mm^2	Mean Defect Length Microns
1	1	119	51.6
1	2	104	42.4
1	3	8	32.8
1	4	6	16.2
1	5	75	38.6
1	6	77	35.8
1	7	13	22.1
1	8	9	19.4
2	2	63	47.6
2	4	27	29.2
2	9	22	38.5
3	3	86	21.5
3	4	78	27.3
3	9	67	33.6
4	2	269	37.4
4	4	13	50.8
4	9	18	34.1
5	2	705	28.2
5	4	58	18.1
5	9	78	17.5
6	2	122	25.0
6	4	106	17.7
6	9	155	21.3

From the data in Table VII it is seen that the defect frequencies in Alloy C19400 after being cold rolled and annealed is reduced by a significant factor. Also, the data shows that there is no significant difference in the defect frequencies between those samples that were annealed prior to cold working and annealing and those which did not have such anneal. This indicates that the anneal in the as-cast condition is not nec ssary for pore healing.

Table VII also shows that by cold rolling and annealing, the defect frequencies in Alloy C71300 and C51000 were also significantly reduced. Alloy C194 + Si also showed a reduction in defect frequency after treatment, although not as great as with the other alloys. However, in the case of Alloy C19400 + Al and the Cu-Al-Si sample, no significant pore healing occurred.

Table VIII below sets forth the pore or defect frequency and mean defect size for spray cast samples of Alloy C51000 and C71300, with and without the nominal addition of 0.5% Al, which were subjected to various treatment conditions. The defect frequency and size were measured in the as-cast condition after milling, after being cold rolled 82% (10% per pass), and after being cold rolled (82%, 10%/pass) and annealed at 700°C for four hours, as indicated in the Table.

TABLE VIII

Pore Sizes and Frequencies

Alloy	Condition	Pore or Defect Frequency Number/mm^2	Mean Defect Size Microns
C510	As Cast	705	7.9/9.1
C510 + AL	As Cast	790	9.7/8.4
C713	As Cast	463	8.0/8.6
C713 + AL	As Cast	368	7.7/8.8
C510	CR 82%	939	19.5
C510	CR 82% + 700°C/4 hrs.	50	24.6
C510 + AL	CR 82%	966	19.6
C510 + AL	CR 82% + 700°C/4hrs.	180	16.8
C713	CR 82%	332	29.8
C713	CR 82% + 700°C/4 hrs.	45	25.0
C713 + AL	CR 82%	427	24.5
C713 + AL	CR 82% + 700°C/4 hrs.	21	30.9

The results set forth in Table VIII show that in the case of Alloys C51000 and C71300, pore or defect frequency was greatly reduced by cold rolling and annealing, irrespective of whether a nominal Al addition had been made. Thus, the addition of Al does not universally inhibit the healing of the pores. Rather, for reasons not known at this time, it has a detrimental effect only in the case of certain alloys such as C19400.

Table IX below sets forth the mechanical properties of spray cast samples, as well as a control sample, of Alloy C71300. The Samples 1 and 2 were spray cast under varying conditions followed by milling of the top and bottom surfaces. The Samples 1 and 2 were then cold rolled to an 87% reduction and annealed at 700°C for three hours. The control sample was conventionally cast using the D.C. (direct chill) casting process and hot rolled after which the top and bottom surfaces were milled. After milling, the control samples were subjected to the same cold roll reduction and anneal as the spray cast samples.

TABLE IX

Alloy C713
Mechanical Properties of 0.026" Guage

Sample	0.2% Yield Strength KSI	Tensile Strength KSI	% Elongation
1	15.0	48	41
2	16.0	50	39
Control	16.5	48	33

From Table IX it is seen that the mechanical properties of spray cast Alloy C71300 at 0.026" guage are equivalent to that of the conventionally cast control sample.

As used herein, the term "yield strength" refers to the strength measured at 0.2% offset. The term "ksi" is an abbreviation for thousands of pounds per square inch.

WHAT IS CLAIMED:

1. A method of treating a spray cast metal deposit to reduce the effects of porosity characterized by:

cold working said deposit to a reduction sufficient to collapse the pores and elongate them in the direction of cold working, and

annealing the cold worked deposit at time and temperature to heal a substantial portion of said defects.

2. The method of claim 1 characterized in that said anneal is at a temperature of at least 450°C for at least 1 hour.

3. The method of claim 1 characterized in that said metal deposit is a copper alloy.

4. The method of claim 1 characterized in that said metal deposit is a copper alloy containing iron.

5. The method of claim 1 characterized in that said metal deposit is a copper alloy containing tin and phosporous.

6. The method of claim 1 characterized in that said metal deposit is a copper alloy containing nickel.

7. The method of claim 1 characterized in that said metal deposit is a copper alloy containing between about 1 to about 3.5% iron, between about 0.03 to about 0.02% zinc, between about 0.01 to about 0.15% phosphorous, and the balance copper.

8. The method of claim 1 characterized in that said metal deposit is a copper base alloy containing between about 3.5 to about 5.8% tin and from about 0.03 to about 0.35% phosphorous.

9. The method of claim 1 characterized in that said metal deposit is a copper base alloy containing from about 23.5 to about 26.5% nickel.

10. The method of claim 1 characterized in that said metal deposit is copper base alloy containing from about 3.5 to about 5.8% tin, from about 0.03 to about 0.35% phosphorous, up to about 0.05% lead, up to about 0.30% zinc, up to about 0.10% iron, and the balance essentially copper.

11. The method of claim 1 characterized in that said metal deposit is a copper alloy containing from about 23.5 to about 26.5% nickel, up to about 1.0% manganese, up to about 1.0% zinc, up to about 0.20% iron, up to about 0.25% lead, and the balance essentially copper.

12. A method of treating a spray cast copper base metal deposit characterized by cold rolling said deposit to a reduction of at least 25% and thereafter annealing said deposit at a temperature of at least 450°Cfor at least 1 hour.

13. The method of claim 12 characterized in that said deposit is cold worked to a reduction of at least 50%.

14. The method of claim 12 characterized in that said anneal is for a time of from about 2 to about 6 hours.

15. The method of claim 14 characterized in that said anneal is at a temperature of from at least about 500°C.

16. A process for producing a copper base alloy characterized by:

a. providing a molten stream of a copper base alloy containing from about 1 to about 3.5% iron, from about 0.01 to about 0.15% phosphorous, from 0.03 to 0.20% zinc and the balance essentially copper,

b. atomizing said molten stream and depositing the atomizing particles onto a moving substrate to form a deposit,

c. cold working said deposit to a reduction of at least 25% and, annealing said deposit at a temperature of at least 450°C for about 1 to about 8 hours.

17. The process of claim 16 characterized in that said cold working is to a reduction of at least 75% and said annealing is at a temperature of at least 500°C for about 2 to about 6 hours.

18. A process for producing a copper base alloy characterized by:

a. providing a molten stream of a copper base alloy containing from about 3.5 to about 5.8% tin and from about 0.03 to about 0.35% phosphorous,

b. atomizing said molten stream and depositing the atomizing particles onto a moving substrate to form a deposit,

c. cold working said deposit to a reduction of at least 25% and, annealing said deposit at a temperature of at least 450°C for about 1 to about 8 hours.

19. A process for producing a copper base alloy characterized by:

a. providing a molten stream of a copper base alloy containing from about 23.5 to about 26.5% nickel,

b. atomizing said molten stream and depositing the atomizing particles onto a moving substrate to form a deposit,

c. cold working said deposit to a reduction of at least 25% and, annealing said deposit at a temperature of at least 450°C for about 1 to about 8 hours.

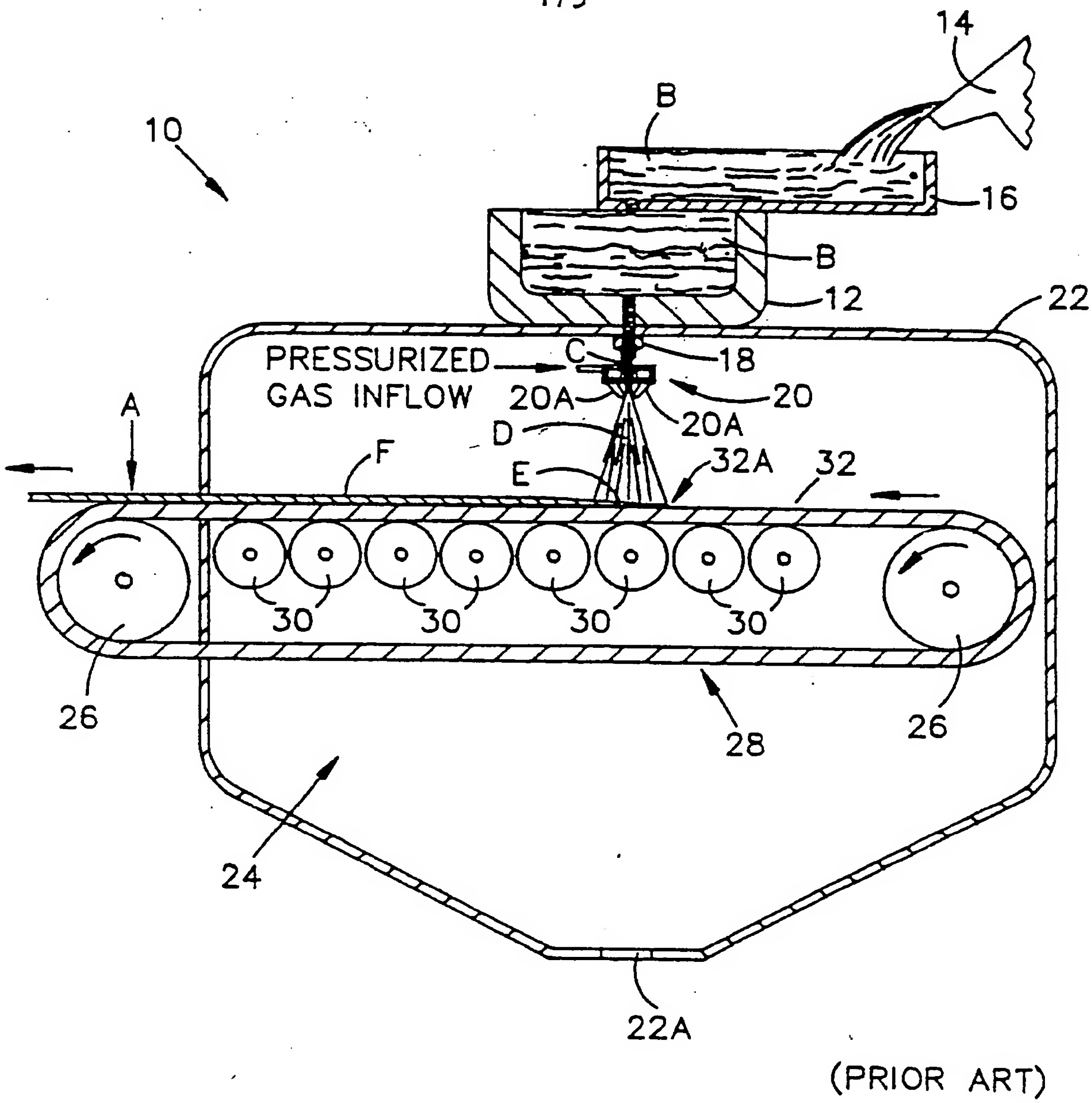
20. A process for producing a copper base alloy characterized by:

a. providing a molten stream of a copper base alloy,

b. atomizing said molten stream and depositing the atomizing particles onto a moving substrate to form a deposit,

c. cold working said deposit to a reduction of at least 25% and, annealing said deposit at a temperature of at least 450°C for about 1 to about 8 hours.

1/3


14
B
10
16
B
12
22
PRESSURIZED
GAS INFLOW
C
18
20A
20
20A
A
D
F
E
32A
32
30
30
30
30
26
28
26
24
22A
(PRIOR ART)

FIG—1

FIG - 2

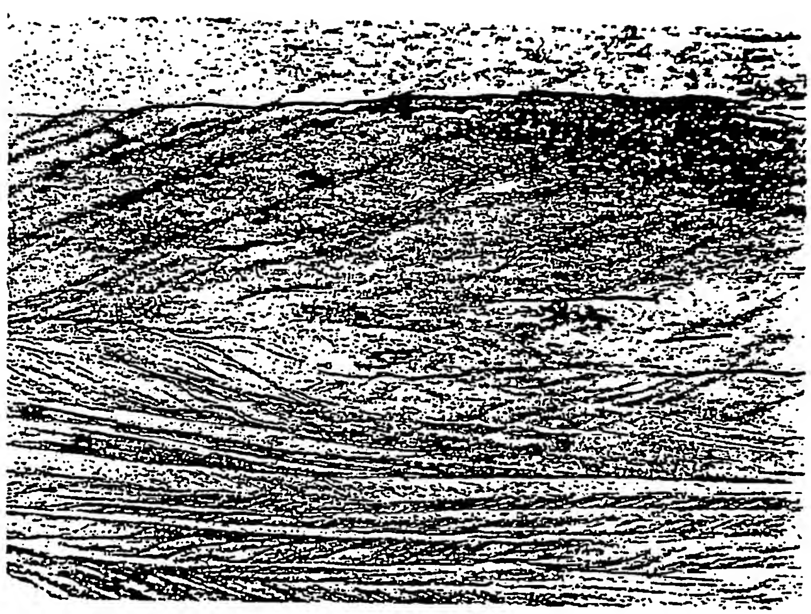


FIG - 3

SUBSTITUTE SHEET

FIG - 4

FIG - 5

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/01737

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC
IPC[5] : B22D 23/00; B22F 9/08; C22F 1/08
U.S.: 148/2,11.5C; 75/338; 164/46

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	148/2,3,11.5C,433,434,435 75/338/339/351; 164/46; 427/422

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, B, RE 31,767 (BROOKS) 18 December 1984 entire document.	1-20
Y	US, A, 3,663,311 (CHIN et al.) 16 May 1972 entire document.	1-20
Y	US, A, 3,775,156 (SINGER) 27 November 1973 entire document.	1-20
Y	US, A, 4,738,712 (SINGER) 19 April 1988 entire document.	1-20
Y	US, A, 4,804,034 (LEATHAM et al.) 14 February 1989 entire document.	1-20
Y	JP, A, 61-119660 (NIPPON MINING) 06 June 1986 abstract.	1-20
Y	JP, A, 62-177160 (SUMITOMO METAL) 04 August 1987 abstract.	1-20
Y	JP, A, 62-214164 (MITSUI MINING) 19 September 1987 abstract.	1-20
A	Metals Handbook, 9th edition, vol. 2, pp. 354-355, 1979.	5,8,10,18

* Special categories of cited documents: [10]
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21 MAY 1990	24 AUG 1990
International Searching Authority	Signature of Authorized Officer
ISA/US	GEORGE WYSZOMIERSKI Veronica Gas - for